

HALFTONE PHASE SHIFTING PHOTOMASK AND BLANKS FOR HALFTONE  
PHASE SHIFTING PHOTOMASK THEREFOR AND A METHOD FOR FORMING  
PATTERN BY USING THE HALFTONE PHASE SHIFTING PHOTOMASK  
BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0001] The present invention relates to photomask used in the production density integrated circuit such as LSI, blanks for photomask for the production of the photomask and a method for forming pattern by using the halftone phase shifting photomask, and in particular to halftone phase shifting photomask by which projected image having fine dimensions can be obtained, blanks for halftone phase shifting photomask for the production of the halftone phase shifting photomask and a method for forming pattern by using the halftone phase shifting photomask.

(2) Description of the Prior Art

[0002] Semiconductor integrated circuits such as LST are produced by repeating the so-called lithographic process in which a photomask is used. Particularly, for the formation of products having fine dimensions, the use of phase shifting photomask such as that described for example in Japanese Patent Laid-Open No. 173744 of 1983 (Showa 58), Japanese Patent Publication No. 59296 of 1987 (Showa 62) and others are studied. Especially, the so-called halftone phase shifting photomask such as that described for example in U. S. P. 4,890,309 attracted the attention of people from a viewpoint of early practical application. Some proposals are made as to the improvement in yield and the structure and material which result in a decrease in cost as being described in Japanese

Patent Laid-Open No. 2259 of 1993 (Heisei 5), Japanese Patent Laid-Open No. 127361 of 1993 (Heisei 5) and others, and making practicable is being proceeded.

[0003] Halftone phase shifting photomask is explained briefly referring to figures. Fig. 1 is an explanatory view showing the principle of halftone phase shifting lithography. Fig. 2 is an explanatory view showing conventional method. Fig. 1 (a) and Fig. 2 (a) are a sectional view of photomask, respectively. Fig. 1 (b) and Fig. 2 (b) show the amplitude of light on photomask, respectively. Fig. 1 (c) and Fig. 2 (c) show the amplitude of light on wafer, respectively. Fig. 1 (d) and Fig. 2 (d) show the strength of light on wafer, respectively. Numerals 11 and 21 designate transparent substrate. Numeral 22 designates 100 % lightproof film. Numeral 12 designates a halftone phase shifting film. Numerals 13 and 23 designate incident rays. Halftone phase shifting film is a film having the function that phase of applied rays which have passed through the film is inverted in fact against phase of applied rays passing through air with the same length of light paths and the optical strength of the former is attenuated against the optical strength of the latter, which is formed of a layer or multiple layers. In a conventional method, as shown in Fig. 2 (a), 100% lightproof film 22 made of chromium and others is formed on substrate 21 made of quartz glass and others, by which a light-transmitting area having a desired pattern is only formed, wherein as shown in Fig. 2 (d), the distribution of optical strength shows the spread of edges so that the resolution is decreased. On the contrary, in the halftone phase shifting lithography, since

the phase of rays which have transmitted halftone phase shifting film 12 of semitransparent film is inverted in fact against phase of rays which have passed through openings of the halftone phase shifting film 12, as shown in Fig. 1 (d), the optical strength in the border of pattern formed on halftone phase shifting photomask becomes 0 on wafer so that the spreading of both edges is suppressed, therefore the solution being improved.

[0004] Special attention should be paid to that in order to obtain the effect of halftone phase shifting photomask, the phase angle and the transmittance of halftone phase shifting film become very important, adding to various characters such as the dimensional tolerances, the positional tolerances and others of pattern formed on the photomask which are requested to conventional photomask, and further that the phase angle and transmittance are determined according to refractive index, coefficient of extinction in the wavelength of applied rays and the thickness of film of a layer or multiple layers forming halftone phase shifting film.

[0005] Generally, the most suitable value for the phase angle is  $180^\circ$ . However, the most suitable value for the transmittance is in the region of 1 through 20% supposing the transmittance in the opening area of halftone phase shifting film is 100%, which is determined according to pattern to be transferred, transferring conditions and others. As to halftone phase shifting photomask, it is requested to set the phase angle and the transmittance to the most suitable values thereof. When values of them deviate from the most suitable value, a proper quantity of the change of applied rays

appears, which results in the lowering of the dimensional tolerance, and the lowering of the focal latitude or allowable extent and others. Accordingly, refractive index, coefficient of extinction, the accuracy of the thickness of film and stability are important needless to say. Figs. 3 and, 4 show the results of simulation made about the effect of transmittance change and phase difference change in the lithography using halftone phase shifting photomask on a change of focal depth, transferring length and best focus.

[0006] Together with miniaturizing pattern to be formed, it is needed to shorten the wavelength of rays used in lithography. As the miniaturization over the so-called 2.5micron design rule proceeds, the practical application of KrF excimer laser (wavelength: 248 nm) starts, and further the length of pattern is miniaturized. In consideration of the above-mentioned conditions, the use of ArF excimer laser is studied. As to a halftone phase shifting film used in a halftone shifting photomask, the development of material is requested which enables the most suitable phase angle and transmittance to also realized for these wavelengths and has the stable refractive index and coefficient of extinction.

[0007] Accordingly, it was proposed to use film containing mainly chromium and including fluorine as disclosed in Japanese Patent Laid-Open No. 110572 of 1995 (Heisei 7) as halftone phase shifting film. This film enables the range of values of suitable phase angle and transmittance against the above-mentioned wavelength to be realized. Further, this film has the advantage of the production of blanks, manufacturing process of mask and others being possible in the same manner

as these of conventional photomask. Therefore, the investigation of this film was begun from the early stage, and practical application was made.

[0008] However, the halftone phase shifting film containing mainly chromium and including fluorine has a problem that by applying rays used in the application of rays such as ArF excimer laser, over a long time, refractive index, and coefficient of extinction, or any of the two of the halftone phase shifting film change(s). Therefore, in case of forming a resist pattern using the halftone phase shifting photomask having the halftone phase-pattern film that contains mainly chromium and includes fluorine, the refractive index and phase angle, or any of the two changes, ever time the halftone phase shifting photomask is used.

[0009] In this case, as is evident from the result of simulation shown in Figs. 3 and 4, even if the phase difference and transmittance slightly change, focusing position, and latitude as well as transferring length change greatly. Namely, this changes result the possibilities that a proper quantity of the change of applied rays, the lowering of dimensional tolerance and the lowering of focal latitude appear every time a photomask is used, and that even in one usage of photomask, these change, which results in a decrease in latitude of pattern forming and the worsening of shape of pattern.

#### BRIEF SUMMARY OF THE INVENTION

[0010] Accordingly, it is an object of the present invention to provide blanks for halftone phase shifting photomask used for the production of halftone phase shifting

photomask in which transmittance change and phase angle change do not appear even if excimer laser for expose is applied to photomask for a long time.

[0011] It is a second object of the present invention to provide a halftone phase shifting photomask in which transmittance change and phase angle change do not appear even if excimer laser for expose is applied to photomask for a long time.

[0012] It is a third object of the present invention to provide a method of forming a pattern using the blanks for halftone phase shifting photomask.

[0013] First type of blanks for halftone phase shifting photomask according to the present invention comprises a halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which heat treatment is given to the halftone phase shifting film, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0014] Second type of blanks for halftone phase shifting photomask according to the present invention comprises a halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which a protective film is provided on the heat-treated halftone phase shifting film, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0015] Third type of blanks for halftone phase shifting photomask according to the present invention comprises a halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which the surface layer of the heat-treated halftone phase shifting is removed by etching the surface, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased, and the transmittance thereof is increased.

[0016] In the first type of blanks for halftone phase shifting photomask, it is desirable that interface disappears from the inside of the halftone phase shifting film by the heat treatment of the halftone phase shifting film.

[0017] In the second type of blanks for halftone phase shifting photomask, it is desirable that the protective film includes at least chromium and fluorine, and the content of fluorine contained in the protective film is lower than the content of fluorine contained in the halftone phase shifting film. Further, it is desired that the protective film is a transparent film.

[0018] First type of halftone phase shifting photomask according to the present invention comprises a pattern of halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which heat treatment is given to the halftone phase shifting film, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0019] Second type of halftone phase shifting photomask according to the present invention comprises a pattern of halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which after the halftone phase shifting film has been formed into a desired pattern, the halftone phase shifting film is heat-treated, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0020] Third type of halftone phase shifting photomask according to the present invention comprises a pattern of halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which a protective layer is provided on the pattern of halftone phase shifting film, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0021] In the fourth type of halftone phase shifting photomask according to the present invention comprises a pattern of halftone phase shifting film including at least chromium and fluorine on a transparent substrate, in which after the halftone phase shifting film has been formed into a desired patter, a protective layer is provided on the whole surface of the photomask, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.



[0022] In the first type of halftone phase shifting photomask, it is desired that after heat-treating halftone phase shifting photomask, a protective film is provided on the heat-treated halftone-shifting film, thereafter the protective film and the halftone phase shifting film are formed into a desired pattern, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0023] Further, in the first type of halftone phase shifting photomask, it is desired that after heat-treating halftone phase shifting film, the heat-treated halftone phase shifting film is formed into a desired pattern, thereafter a protective film is provided on the whole substrate, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0024] In the second type of halftone phase shifting photomask, it is desired that after heat-treating the halftone phase shifting film formed into a desired pattern, a protective film is provided on the whole surface of photomask, by which a change of optical characteristic of the halftone phase shifting film appearing in applying excimer laser for exposure to the halftone phase shifting film is decreased.

[0025] In the first and second types of halftone phase shifting photomasks, it is desired that by heat-treating halftone phase shifting film, the interface disappears in the inside of the halftone phase shifting film by heat-treating the halftone phase shifting film.

[0026] In the third and fourth types of halftone phase shifting masks, it is desired that a protective film includes at least chromium and fluorine, and the content of fluorine contained in the protective film is lower than the content of fluorine contained in the halftone phase shifting film. Further, it is desired that the protective film is transparent.

[0027] Further, in any of the above-mentioned halftone phase shifting photomask, it is also desired that when forming a pattern, a size of pattern is made smaller than the desired size.

[0028] Further, the present invention a method of forming a pattern includes a method of forming a pattern using the above-mentioned halftone phase shifting photomask.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Fig. 1 is a view for showing the principle of halftone phase shifting lithography.

[0030] Fig. 2 is a view for showing conventional lithography against Fig. 1.

[0031] Fig. 3 is a view for showing that focal depth and transferring length are affected by phase difference change in the lithography in which a halftone phase shifting photomask is used.

[0032] Fig. 4 is a view for showing that focal depth and best focus change are affected by a change of phase difference change, in the lithography in which a halftone phase shifting photomask is used.

[0033] Fig. 5 is a view for showing a state in which phase difference and transmittance are changed by applying excimer

laser to a halftone phase shifting photomask having the halftone phase shifting film containing chromium and fluorine.

[0034] Fig. 6 is a brief view of irradiation device.

[0035] Fig. 7 is a view for showing that the spectrum analyzed from reflectance of X-rays (of after Fourier transform) is changed by applying excimer laser to a halftone phase shifting photomask having the halftone phase shifting film containing chromium and fluorine, in which Fig. 7(a) shows the spectrum analyzed from reflectance of X-rays of before the applying of excimer laser to the halftone phase shifting photomask, and Fig. 7(b) shows the spectrum analyzed from reflectance of X-rays of after the applying of excimer laser to the halftone phase shifting photomask.

[0036] Fig. 8 is a view for illustrating the processes in which blanks for halftone phase shifting photomask are produced and then a halftone phase shifting photomask of example 1 is obtained by processing the blanks for halftone phase shifting photomask.

[0037] Fig. 9 is a view for showing the transmittance change due to applying excimer laser to a halftone phase shifting photomask having halftone phase shifting film of Example 1.

[0038] Fig. 10 is a view for illustrating the process for producing a halftone phase shifting photomask of Example 2.

[0039] Fig. 11 is a view for showing the phase difference change and the transmittance change due to applying excimer laser to a halftone phase shifting photomask having halftone phase shifting film of Example 1.

[0040] Fig.12 is a view for showing the phase difference change and the transmittance change due to applying excimer laser to a halftone phase shifting photomask having halftone phase shifting film of Example 4.

#### DETAILED DESCRIPTION

[0041] In the present invention, for blanks for a halftone phase shifting photomask having a halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced when applying excimer laser to the halftone phase shifting film is decreased by treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C.

[0042] Further, in the present invention, for blanks for halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film is increased, by treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C, and then removing the surface of the heat-treated film by etching the surface.

[0043] Further, in the present invention, for blanks for halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer

laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film is increased, by treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C, then removing the surface of the heat-treated film by etching the surface, thereafter coating the halftone phase shifting film with a protective film.

[0044] Further, in the present invention, for blanks for halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, by coating the halftone phase shifting film with a protective film, thereafter treating the halftone phase shifting film with the protective film with heat at a temperature of between 250°C and 500°C.

[0045] Further, in the present invention, as to blanks for halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film is increased, by coating the halftone phase shifting film with a protective film, then treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C, thereafter removing the surface of the heat-treated film by etching the surface .

[0046] In the above-mentioned blanks for halftone phase shifting photomask, it is desirable that the surface of halftone phase shifting film which has been heat-treated contains at least chromium and the content of fluorine contained in the surface thereof is lesser than that contained in the inside thereof.

[0047] Further, in the above-mentioned blanks for halftone phase shifting photomask, it is desirable that the protective film contains at least chromium, and the content of fluorine contained in the protective film is lesser than that contained in the halftone phase shifting film.

[0048] Further, in the above-mentioned blanks for halftone phase shifting photomask, it is desirable that the interface existing in the halftone phase shifting film disappears by the above-mentioned heat-treatment.

[0049] Blanks for halftone phase shifting photomask of the present invention is produced by using the above-mentioned blanks for halftone phase shifting photomask, in which the halftone phase shifting photomask can be obtained by making patterning of the halftone phase shifting film after the above-mentioned treatment

[0050] In the present invention, for a halftone phase shifting photomask having a halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, by treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C, then by forming the heat-treated

halftone phase shifting film into a pattern, thereafter forming a protective film on the whole surface of the halftone phase shifting film.

[0051] Further, in the present invention, for a halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, the halftone phase shifting film with heat at a temperature of between 250°C and 500°C is treated, and then the surface of heat-treated film is removed by etching the surface and that the halftone phase shifting film is formed into a pattern. Thereafter, a protective film is formed on the whole surface of halftone phase shifting photomask, by which a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film is increased.

[0052] Further, in the present invention, in halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film is increased by making patterning of the halftone phase shifting film, then treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C.

[0053] Further, in the present invention, in a halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent

substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film, by making patterning of the halftone phase shifting film, then treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C, removing the surface of the heat-treated halftone phase shifting film.

[0054] Further, in the present invention, for a halftone phase shifting photomask having halftone phase shifting film including at least chromium and fluorine on a transparent substrate, a change of optical property of the halftone phase shifting film produced in applying excimer laser to the halftone phase shifting film is decreased, and the transmittance of halftone phase shifting film is increased by making patterning of the halftone phase shifting film, then treating the halftone phase shifting film with heat at a temperature of between 250°C and 500°C and removing the surface of film by etching the surface, to form a protective film on the whole surface of halftone phase shifting photomask.

[0055] In the above-mentioned photomask, it is desirable that the surface of the protective film contains at least chromium and that the content of fluorine contained in the protective film is lesser than that contained in the halftone phase shifting film.

[0056] Further, in the above-mentioned halftone phase shifting photomask, it is desirable that the protective film is transparent.



[0057] Further, in the above-mentioned halftone phase shifting photomask, it is desirable that the interface existing in the halftone phase shifting film disappears by the above-mentioned heat-treatment.

[0058] Further, in the above-mentioned halftone phase shifting photomask, it is desirable that when forming pattern, a size of pattern is made smaller than desired size.

[0059] Then, the reason why the above-mentioned construction is employed in the present invention is explained.

[0060] Figs. 5 (a), (b) show a state in which phase difference and transmittance are changed by applying excimer laser to a halftone phase shifting photomask having the halftone phase shifting film containing chromium and fluorine, in which phase difference change and transmittance change of halftone phase shifting film against total amount of irradiated energy is shown, in case that an irradiation device shown in Fig. 6 was used, in which ArF excimer laser beam 2 (thereafter, it is called briefly "laser") was applied to halftone phase shifting film 5 from the side of glass substrate 4 disposed in a sample chamber 3 on the condition that pulse energy is  $0.2 \text{ mJ/cm}^2$  /pulse, repeated frequency is 1 kHz, and atmosphere of irradiation is the atmosphere, wherein measurement of phase difference and transmittance was made by means of "MPM193 phase difference measuring instrument" manufactured by LSER TECK Co..

[0061] In order to investigate the cause of phase angle change and transmittance change of halftone phase shifting film containing at least chromium and fluorine being changed

produced according to the above-mentioned application of ArF excimer laser, the compositions of the above-mentioned halftone phase shifting film before and after applying irradiated rays to the halftone phase shifting film were analyzed by the X-ray photoelectron spectroscopy (XPS). The result of analysis is shown in Table 1. The numerical values shown in Table 1 show ratio (%) of atoms existing in the halftone phase shifting film, wherein irradiation of ArF excimer laser to the halftone phase shifting film is made on the condition that pulse energy is 0.2 mJ/cm<sup>2</sup> /pulse, repeated frequency was 1 kHz, and atmosphere of irradiation was the atmosphere. X-ray photoelectron spectroscopy was made using "ESCALAB210" manufactured by VG SCIENTIFIC CO. As to measurement of the composition of halftone phase shifting film of the inside of it, halftone etching of the halftone phase shifting film was made by Ar ion beam, then the analysis thereof was made.

Table 1

		Cr	F	C	O
The surface of Film	Before exposure	14	27	31	28
	After exposure	14	17	34	35
The inside of Film	Before exposure	25	55	10	10
	After exposure	25	55	10	10

[0062] As is apparent herein, a great change of the composition of halftone phase shifting film produced by applying ArF excimer laser to the halftone phase shifting film is not found inside the film, while a change of nature of the film that the amount of fluorine is decreased, and the amount of oxygen is increased is found in the surface of the film.

[0063] Further, Fig. 7 shows the result obtained by analyzing the structure of the halftone phase shifting film in before and after applying rays to the film from X-ray reflectance. In spectrum which has been Fourier-transformed, a sharp peaks appears with distance 31 nm in before applying rays to the film, which shows that the halftone phase shifting film is composed of four layers having the thickness of film 31 nm, respectively. The structure of film composed of layers is caused by that forming of film was made dividing the process of forming of film into four. In after applying rays to the film, these peaks are weakened, which shows that atoms move by applying rays to the film, which results the disappearance of the interface of film.

[0064] When the interface exists in a film, an incident rays are reflected from the interface, as the number of the interfaces is increased, the ratio of reflected light from the interfaces is increased, while the amount of transmitting light is decreased. The above-mentioned disappearance of the interface gets rid of the reflection of light from the interface, so that the transmittance of the halftone phase shifting film is increased. Namely, it is thought that the main cause of the above-mentioned phase difference change and

transmittance change produced according to the application of rays to the film is the disappearance of the interface.

[0065] On the other hand, it is thought that a decrease in the amount of fluorine in the surface of the film produces the decrease in the transmittance of the film. It is thought that the above-mentioned phase difference change and transmittance change produced by rays applied to the film include the phase difference change and transmittance change caused by a change of the nature of film. However, since these phase difference change and transmittance change are the reverse to the phase difference change and transmittance change caused by the reflection of rays from the interface, these changes are not found in Fig.5.

[0066] Accordingly, in the present invention, in a halftone phase shifting photomask having a halftone phase shifting film containing at least chromium and fluorine, before the photomask is used for the exposure, heat-treatment is made to the halftone phase shifting photomask in such a manner that atoms included in the film are dispersed so that the interface is disappeared. Further, since the heat treatment makes fluorine contained in the surface of film evaporate to decrease the transmittance, in order to prevent this, the surface of film in which fluorine has been evaporated is removed by etching the surface, by which the transmittance of film is adjusted to an amount e needed essentially.

[0067] When fluorine is evaporated from the surface of film by the above-mentioned heat treatment so that the concentration of fluorine contained in the surface of film is kept to a suitable amount, the surface of film changes into a

natural protective film formed naturally by the heat treatment. The natural protective film shows the effect that the phase difference change and the transmittance change of the film are controlled.

[0068] Then, further, the present invention can take a form in which a protective film for preventing the change of the above-mentioned nature of film is provided on the surface of halftone phase shifting film. When the amount of fluorine contained in the surface of film is much, as in the surface of film of after the surface of film has been etched, as shown in Fig.1, the nature of film in the neighborhood of the fsurface of film is changed according to the nature of the surface of film. By providing such a structure for preventing a change of the nature of film peculiar to the film portion near the surface of film, phase angle change and transmittance change produced by applying rays to the film laser according to applying can be controlled to be the normal transmittance in the same manner as the above-mentioned case.

[0069] In order to omit the process of etching the surface of film, a halftone phase shifting film can be deposited in such a manner that the concentration of fluorine contained in the halftone phase shifting film becomes higher, so that the defined transmittance as well as the amount of fluorine can be controlled after heat-treating the film.

[0070] As the protective film, transparent films against rays applied to films such as  $\text{SiO}_2$  film are desirable. In these films, a change in the surface shown in Table 1 is not only produced, but also plays a role as the protective film with which a change of quality in which the amount of fluorine

is decreased as above-mentioned and the amount of oxygen is increased is prevented. Accordingly, the phase difference change and the transmittance change of the halftone phase shifting photomask produced by applying of rays to the film can be prevented.

[0071] There are given as protective films transparent films as  $MgF_2$ ,  $CaF_2$ ,  $LiF_2$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ ,  $HfO_2$ ,  $Ta_2O_5$ ,  $ZnO$ ,  $MgO$ , and  $W_2O_5$  in addition to the above-mentioned metal oxide  $SiO_2$ . As to these transparent, if the halftone phase shifting film has been deposited on a transparent substrate, the desired effect can be obtained, even if the transparent films are deposited in any process in the producing process of photomask.

[0072] Further, the transparent film may be rays-semitransparent to irradiated rays. In this case, it is desirable that semitransparent film is deposited before forming photomask blanks into desired patterns, wherein the semitransparent protective film is formed into the same patterns as that of halftone phase shifting film at the same time in forming halftone phase shifting film into the desired pattern or in another process.

[0073] However, anyway, halftone phase shifting film in these cases should be deposited in such a manner that the desired relation on the transmittance and phase difference between opened areas and patterned areas of the halftone phase shifting is formed. Further, when it is expected that protective film is deposited on the cross section of parts of halftone phase shifting film having patterns, in such a case as a protective film is formed after the desired pattern was

made beforehand. It is considered that a change of size of transferred pattern to resist is caused by depositing of protective film on the cross section of halftone phase shifting film. It is desirable to form a pattern adding the change of pattern caused by depositing of protective film on the cross section of halftone phase shifting film.

[0074] Further, in a case where the halftone phase shifting film including at least chromium and fluorine is formed into a multiplayer film, it is effective that a film in which a change of the property of the surface of film by applying rays to the surface of film is hard to be produced. In this case, in case of the film containing at least chromium and fluorine, since a phenomenon such as the amount of fluorine is decreased and the amount of oxygen is increased occurs intensively, as the content of fluorine increase. Therefore, in this case, it is desirable to dispose a film having a small amount of fluorine.

[0075] Finally, each of the heat-treatment and the forming of protective film shows a sufficient effect for suppressing a change in transmittance or phase angle of the halftone phase shifting film containing at least chromium and fluorine produced by the application of ArF excimer laser to the film, independently, as above-mentioned. However, both the heat-treatment and the forming of protective film can be applied. In this case, even if which of the heat-treatment and the forming of protective film is made first, difference in the effect thereof cannot be found. Further, respective treatment can be made in any process in the manufacturing process of photomask.

[0076] In such a way, the transmittance and the phase difference, according to the present invention, can be stabilized against the application of ArF excimer laser and other to the halftone phase shifting film by making the interface disappear by the heat-treatment for the halftone phase shifting photomask having halftone phase shifting film containing at least chromium and fluorine disposed on a transparent substrate.

[0077] Further, for the halftone phase shifting photomask, the protective film on the surface of halftone phase shifting film prevents a change of the property of the surface of the film from being produced by the application of ArF excimer laser and others to the film, so that the transmittance and phase difference can be stabilized.

[0078] Modifying of the halftone phase shifting film or the forming of protective film reduces in transmittance change and phase angle change arisen in storage of photomask, or under usage, wherein the problem is solved and reduced that the suitable amount of rays is changed, the accuracy of size is lowered, and the focal latitude is decreased, so that the shape of pattern is worsened, every time a photomask is used.

#### Example 1

[0079] Referring to Fig.8, an example of blanks for halftone phase shifting photomask and a halftone phase shifting photomask of the present invention is explained,

[0080] As shown in Fig. 8 (a), a halftone phase shifting film 102 containing chromium and fluorine was formed on a synthetic quartz substrate 101 polished optically and rinsed sufficiently, under the under-mentioned conditions, by which



blanks for halftone phase shifting photomask 103 was obtained, wherein the thickness of formed halftone phase shifting film 102 was 130 nm.

Conditions:

Film deposition equipment: DC magnetron sputter equipment

Target: Metal chromium

Gas and the flow rate thereof: Argon gas 76 sccm + carbon tetrafluoride gas 245 sccm

Pressure of sputter: 3.0 mm

Electric current of sputter: 5.5 ampere

[0081] Halftone phase shifting films 102 having the same thickness were deposited on the same thickness under the same conditions, and the halftone phase shifting films are formed into a pattern by conventional lithography method, by which samples for measurement of phase difference and transmittance 104 were formed, as shown in Fig. 8 (b). As a result of measurement of phase difference and transmittance under wave length 193 nm of halftone phase shifting film with the phase contrast meter made by LASER TECK Co., Ltd., "MPM193" put on the market, phase difference of 164 ,and transmittance of 11 % was obtained.

[0082] Then, the heat-treatment was given to the blanks 103 for halftone phase shifting photomask, by which as shown in Fig.8 (c), blanks 105 for halftone phase shifting photomask were obtained, in which a change of optical property produced when using a photomask was reduced. Table 2 shows conditions

of heat-treatment and the transmittance in wave length 193 nm of after the heat-treatment.

Table 2

Temperature (°C)	Time (Hr)	Atmosphere	Transmittance (%)
200	6	Air	11
300	5	Air	6
300	5	N <sub>2</sub>	8

[0083] After ArF excimer laser beam of wave length 193 nm was applied to the blanks, the measurement of phase difference and transmittance in wave length 193 nm was measured, under the under-mentioned conditions.

Light source: ArF excimer

Irradiation atmosphere: Nitrogen: Oxygen = 80 : 20

Pulse energy: 0.2 mJ/cm<sup>2</sup>/pulse

[0084] In this time, the irradiation of laser was made from the side of substrate 101. Fig. 9 shows the result of the measurement of phase difference and transmittance. The upper and lower limits of transmittance change were within  $\pm 0.3$  %, wherein the respective values are shown by the dotted lines in Fig. 9. In a case where the heat-treatment is not given to the blanks, transmittance change reaches +1.4 % at 10kJ/cm<sup>2</sup> of total irradiation energy. Then, in a case where the heat-treatment was given to the blanks at 200°C, the difference

between a case where the heat-treatment is not given to the blanks is not found. However, in a case of the heat-treatment was given to the blanks at 300°C, even in 10kJ/cm<sup>2</sup> of total irradiation energy, transmittance change is within  $\pm 0.3$  %. From this fact, it is seen that a change of optical property is reduced.

[0085] It was confirmed that the interface existing in the halftone phase shifting film was made disappear by the heat-treatment, by the analysis made in the direction of the thickness by XPS. Namely, that transmittance change of after heat-treatment as shown in Fig.9 is small is based on that the interface is made disappear by the heat-treatment accompanied with diffusion of atoms.

[0086] In the same heat-treatment of 300°C, the difference in transmittance change between the heat-treatment made in air and the heat-treatment made in Nitrogen atmosphere was not found. However, the difference in the initial transmittance between the two was found. Namely, as shown in Table 2, difference in the initial transmittance is lowered from 11 % to 8 % in Nitrogen atmosphere. However, difference in the initial transmittance is lowered to 6 %. Fig. 3 shows the result of analysis by XPS of after heat-treatment.

Table 3

			Cr	F	C	O
200 in Air	The surface of Film	Before Irradiation	14	23	23	40
		After Irradiation	15	20	18	47
	The inside of Film	Before Irradiation	25	55	10	10
		After Irradiation	25	55	10	10
300 in Air	The surface of Film	Before Irradiation	20	0	8	72
		After Irradiation	22	0	4	74
	The inside of Film	Before Irradiation	25	53	5	17
		After Irradiation	25	53	5	17
300 in N <sub>2</sub>	The Surface of Film	Before Irradiation	24	2	3	71
		After Irradiation	18	2	0	80
	The Inside of Film	Before Irradiation	25	53	5	17
		After Irradiation	25	53	5	17

[0087] The composition of the inside of a sample not yet irradiated changes scarcely as compared with that of before annealing (Table 1). However, it was found that when the film is annealed when the film is annealed at 300°C, fluorine was released from the surface of film, while oxygen enters the surface of film. From the estimate about an area from which fluorine is released, it was found that in case of the heat-treatment made at 300°C in air, fluorine was released from the

depth of 30 nm from the surface of film. In case of the heat-treatment made in the nitrogen atmosphere, fluorine was released from the depth of 10 nm from the surface of film. Further, the oxidation of the surface took place from the same depth. From this fact, it is found that the lowering of initial transmittance is caused by the amounts of fluorine and oxygen contained in the film, and that as the amount of released fluorine from the film and the extent of the surface oxidized are increased, the initial transmittance is decreased. It is thought that these amounts are determined by amounts of oxygen contained in the atmosphere in which the heat-treatment is made.

[0088] It is found that thereafter, blanks for halftone phase shifting photomask has been heat-treated at 300°C in such a manner, the optical property of film becomes unchanged even if ArF excimer laser is applied to the heat-treated. Therefore, in case where halftone phase shifting film of the blanks is formed into a pattern to form a photomask, thereafter forming of pattern to resist is carried out, phase difference change and transmittance change produced in the process of transferring of pattern are lessened to improve practicability.

[0089] Then, a process of processing the blanks for halftone phase shifting photomask into a photomask by forming the halftone phase shifting film into a pattern is explained.

[0090] As shown in Fig. 8 (d), electric beam resist "ZEP7000" (manufactured by NIHON ZEON Co., Ltd.) was applied on blanks 105 for halftone phase shifting photomask in such a manner that the thickness of film comes to 300 nm after being

baked, then was baked at 110°C for 20 minutes to obtain electric beam resist film 106. Further, the latent image of a desired pattern was obtained by means of electric beam writing system for photomask. Thereafter the halftone phase shifting film was developed by special developing solution ZED 500. Therefore, a desired resist pattern 107 is obtained.

[0091] Reactive ion etching was made through the resist pattern 107 as pattern under the under-mentioned conditions, by which dry etching of halftone phase shifting film 102 was made.

Conditions:

Etching equipment: Parallel Flat Plate Reactive Ion Etcher  
Gas and the flow rate thereof: dichloromethane 30 sccm +  
oxygen 60 sccm

Pressure of etching: 200 mTorr

Power of etching: 300 Watt

[0092] After the completion of etching, unnecessary part of resist was removed by treating the surface of film by ozone gas while applying ultraviolet rays to the film, so that halftone phase shifting photomask 108 was obtained as shown in Fig. 8 (e).

[0093] Since the obtained halftone phase shifting photomask 108 was produced by using blanks for halftone phase shifting photomask with the stable optical property as shown in Fig. 9, phase difference change and transmittance produced in the process of transferring of pattern were lessened to improve the practicability.

Example 2

[0094] Then, referring to Fig. 10, an example of halftone phase shifting photomask of the present invention is explained.

[0095] As shown in Fig. 10 (a), a halftone phase shifting film 202 containing chromium and fluorine was formed on a synthetic quartz substrate 201 polished optically and rinsed sufficiently, in the same sputtering method, as in Example 1, by which blanks 203 for halftone phase shifting photomask was obtained, wherein the thickness of formed halftone phase shifting film 202 was 130 nm.

[0096] As shown in Fig. 10 (b), electric beam resist "ZEP7000" (manufactured by NIHON ZEON Co., Ltd.) was then applied on blanks 203 for halftone phase shifting photomask in such a manner that the thickness of film comes to 300 nm after being baked, then was baked at 110 for 20 minutes to obtain electric beam resist film 204. Further, the latent image of a desired pattern was obtained by means of electric beam writing system for photomask, and then the halftone phase shifting film was developed by special developing solution ZED 500 so that a desired resist pattern 205 was obtained.

[0097] Reactive ion etching was made through the resist pattern 205 as pattern under the under-mentioned conditions, by which dry etching of halftone phase shifting film 202 was made.

Conditions:

Etching equipment: Parallel Flat Plate Reactive Ion Etcher

Gas and the flow rate thereof: dichloromethane 30 sccm +  
oxygen 60 sccm

Pressure of etching: 200 mm

Power of etching: 300 Watt

[0098] After the completion of etching, unnecessary part of resist was removed by treating the surface of film by ozone gas while applying ultraviolet rays to the halftone phase shifting film, so that halftone phase shifting photomask 208 was obtained as shown in Fig. 10 (c).

[0099] Then, the halftone phase shifting photomask 206 was rinsed sufficiently, and then the heat-treatment was given to the halftone phase shifting film in the same manner as in Example 1, by which a halftone phase shifting photomask 207 is obtained. Conditions of the heat-treatment were 300°C and atmosphere was atmosphere in air.

[00100] Since the optical property shown in Fig.5 was made beforehand for the obtained halftone phase shifting photomask 207 to reach the stable area of optical property, phase difference change and transmittance produced in the process of transferring of pattern are lessened to improve the practicability.

#### Example 3

[00101] Then, another examples of blanks for halftone phase shifting photomask and halftone phase shifting photomask of the present invention are explained.

[00102] A halftone phase shifting film containing chromium and fluorine was formed on a synthetic quartz substrate polished optically and rinsed sufficiently, in the same



sputtering method, as in Example 1, wherein the thickness of formed halftone phase shifting film was 160 nm.

[00103] The halftone phase shifting film was heat-treated at 300°C in air, and then the surface of film was removed by plasma etching. Conditions of plasma etching were the same as in Example 3.

Conditions:

Etching equipment: Parallel Flat Plate Reactive Ion Etcher  
Gas and the flow rate thereof: dichloromethane 30 sccm +  
oxygen 60 sccm

Pressure of etching: 100 mTorr

Power of etching: 400 Watt

[00104] The measurement of phase difference and transmittance at wavelength 193 nm in the halftone phase shifting film was made by the phase difference meter for phase shifting photomask "MPM 193 (manufactured by LASER TECK Co., Ltd.) put on the market Phase. The measure value of phase difference was about 184° and the measured value of transmittance was 12%.

[00105] After ArF excimer laser beam of 193 nm was applied to the blanks for halftone phase shifting photomask under the under-mentioned conditions, phase difference and transmittance at wavelength 193 nm were measured, wherein conditions of irradiation of laser were the same as in Example 1.

[00106] The irradiation of laser was made from the side of substrate. Fig. 11 shows the results thereof. It is found that phase difference change and transmittance change depending on

total amounts of irradiation energy are smaller as compared with these not yet irradiated.

[00107] Then, in the same manner as in Example 1, halftone phase shifting film of the blanks for halftone phase shifting photomask was formed into a pattern to produce a photomask.

[00108] The obtained halftone phase shifting photomask is shown in Fig. 11. Since the production of the halftone phase shifting photomask was carried out using blanks for halftone phase shifting with the stable optical property, phase difference change and transmittance produced in the process of transferring of pattern are lessened to improve the practicability.

#### Example 4

[00109] Then, referring to Fig. 10, further another examples of blanks for halftone phase shifting photomask and halftone phase shifting photomask of the present invention are explained.

[00110] A halftone phase shifting film containing chromium and fluorine was formed on a synthetic quartz substrate polished optically and rinsed sufficiently, in the same sputtering method as in Example 1, wherein the thickness of formed halftone phase shifting film was 160 nm.

[00111] The halftone phase shifting film was heat-treated at 300°C in air, and then the surface of film was removed by plasma etching. Conditions of plasma etching were the same as in Example 1.

[00112] Further, a protective film having the concentration of fluorine lower than that contained in the inside of film was formed on the above-mentioned halftone phase shifting film

under the under-mentioned conditions, by which blanks for halftone phase shifting photomask were obtained, wherein the thickness of the halftone phase shifting film was 30 nm.

Conditions:

Film deposition equipment: DC magnetron equipment

Target : metallic chromium

Pressure of sputter: 3.0 mm

Electric current of sputter: 2.0 ampere

[00113] Phase difference and transmittance at wave length 193 nm in the halftone phase shifting film are measured by the phase difference meter for phase shifting photomask "MPM 193" (manufactured by LASER TECK Co., Ltd.) put on the market Phase. The measure value of phase difference was about  $183^\circ$  and the measured value of transmittance was 10%.

[00114] After ArF excimer laser beam of 193 nm was applied to the blanks for halftone phase shifting photomask under the under-mentioned conditions, phase difference and transmittance at wave length 193 nm were measured, wherein conditions of irradiation of laser were the same as in Example 1, 3.

[00115] In this case, the application of laser to the halftone phase shifting film was made from the side of substrate. Fig. 12 shows the result thereof, wherein the result of Example 3 is shown together with the result of Example 4. The difference between phase difference changes of the two was not found. For transmittance, it was found that in a case where a protective film was provided on the halftone

phase, the transmittance rises in a region where the amounts of irradiation is low, but thereafter is reduced.

[00116] Then, in the same manner as in Example 1, halftone phase shifting film of the blanks for halftone phase shifting photomask was formed into a pattern to produce a photomask.

[00117] The obtained halftone phase shifting photomask is shown in Fig. 12. Since the production of halftone phase shifting photomask is carried out using blanks for halftone phase shifting with the stable optical property, phase difference change and transmittance produced in the process of transferring of pattern are lessened to improve the practicability.

[00118] As apparent from the above-mentioned description, a halftone phase shifting photomask and blanks for halftone phase shifting photomask of the present invention, a change in the property of halftone phase shifting film produced by the application of laser beam to the film is produced before the film is used practically so that the property thereof is stabilized, or a protective film is provided on the halftone phase shifting film, or the two means are used together, by which phase difference change and transmittance change produced when using the photomask can be reduced. As a result, the most suitable halftone phase shifting photomask with the excellent practicability can be obtained.